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GRAPHITIZATION OF CAST IRON AS AN ELECTRO-BIOCHEMICAL
PROCESS IN ANAEROBIC SOILS

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WARREN P. IVERSON
U. S. Army Biological Laboratories

GRAPHITIZATION OF CAST IRON AS AN ELECTRO-BIOCHEMICAL PROCESS IN ANAEROBIC SOILS

/Following is a translation of an article by Dr. C. A. H.
von Wolzogen Kühr and L. S. van der Vlugt in the Dutch-
language periodical Water, Vol 18, No. 16, The Hague,
3 August 1934, pages 147-165./

Introduction.

With the continuing expansion of gas and water systems, both in number and in size, coupled with increasing use of cast iron as pipeline material, the results of graphitization of the pipes has not only seriously menaced the reliability of service, but also occasioned a considerable increase in financial loss. The result has been a search along various lines for means if not of preventing this evil at least of limiting it as much as possible.

The insulating materials in general use which have been resorted to up to now in order to protect the iron pipes externally against corrosive soil influences have not yet led to an effective result. To be able to combat the danger of corrosion of pipelines in the ground with effective measures the first requirement is an insight into the nature of iron corrosion. Since the literature referred to and discussed below on the cause of the corrosion of cast-iron pipelines in our opinion could not be correct, a renewed investigation was indicated.

During the past five years at the laboratory of the Provincial Waterworks of North Holland this investigation of the cause of graphitization of cast iron has been carried out anew from the very beginning.

The results and the resulting opinions are set down in the following chapters.

Chapter I. Review of the Literature.

According to Dipl. Eng. P. Medinger (1) /For this and later references, see the bibliography/ the cause of graphitization of cast iron must be sought in solution of the iron in accordance with electro-chemical theory (page 74). Particular attention is called by Medinger to the action of gypsum (page 75), which, where carbonic acid is present in the soil, through union of HCO_3 -ions with Ca-ions of the sulfate into undissociated calcium carbonate, promotes dissociation of the carbonic acid into H and HCO_3 -ions. By this increase in H-ions, according to him, the aggressive influence of the soil is heightened. The calcium sulfate thus not only favors the corrosion of iron by acting as an electrolyte, but also by increasing the H-ion concentration (derived from the carbonic acid) in the soil. From this we should have to conclude that according to Medinger the hydrogen-ion concentration of the underground water must in general be expected to be high in the soils of sulfate content described above, but this is in disagreement with our observation, for in such soils, in which cast iron is much graphitized, we always found a pH value not far from 7, which can hardly be said to represent a high hydrogen-ion concentration. The cause assigned by Medinger for graphitization of cast-iron pipes in clay soils containing gypsum therefore cannot be of general validity. The question of why according to Medinger cast iron corrodes more in a clay soil, which prevents access of oxygen, than in a sandy soil with access of air, is answered by him as follows. The iron is converted by the solution pressure into Fe-ions, which would be carried away as a result of changes in the underground water level, whereas, according to him, diffusion through the clay would readily occur. Since in the absence of air no resistant layer of rust can form, solution of the iron by the solution pressure would continue, so that in this way corrosion would therefore occur more rapidly than in the presence of air. This seems to us to be in conflict with point 3 of his summary of results on page 90, where he says that clay has the property of stubbornly retaining water and salts and thus brings it about that the corrosion of iron proceeds uninterruptedly. Why on the one hand the salts would not be diffused away through the clay and on the other hand the Fe-ions would be very readily so diffused is not clear. The conclusion from this view would be that the corroding iron is left with a negative charge by the positive iron ions that are being diffused away, but this is senseless from the electro-chemical standpoint.

In a study of corrosion it is obvious that a study must be made of the corrosion products in order to determine the nature of the process. Medinger does speak on page 90 of a mixed iron oxide formed as a product of corrosion, but this cannot be the result of a complete study, since the iron sulfide that always occurs in the graphitization process is not mentioned by him. On pages 73 and 74 the author mentions that the affected pipes lay in grayish yellow clay with pockets of gypsum, while the clay was rich in calcium bicarbonate and the ground showed black layers rich in humus. It will later appear that these soil characteristics form

a strong indication that an iron corrosion process has taken place in which sulfate reduction plays an important part. In this connection, the dark substance encountered presumably consists in part of iron sulfide, which is an unmistakable indication of sulfate reduction in the soil.

In our experience of the anaerobic iron corrosion process, in opposition to Medinger's view, according to which the ferro-ions are diffused away, we found the iron that originally went into solution left behind in the immediate neighborhood of the corroded pipe in the form of precipitated iron compounds. This precipitate always contained a considerable quantity of iron sulfide.

It is a striking fact that in the electrochemical representation of the corrosion process the important depolarization to eliminate the cathodic hydrogen, necessary in order to make possible an uninterrupted process, is not even mentioned.

There is the further fact that Medinger's theory of the graphitization of cast iron can give no explanation for the quite general occurrence of iron sulfide as a product of corrosion, so that in our opinion his electrochemical explanation cannot be correct.

The most conspicuous gap in Medinger's study of the cause of graphitization of cast iron in the ground is the lack of any experiment in which he reproduces the process of graphitization of cast iron, according to the cause given by him, in the laboratory.

Although Dip. Eng. R. Stumper (2) deals with the graphitization of cast iron in his article, his study does not fall directly within the bounds of our concern, since no case of cast iron corrosion under anaerobic soil influences is involved. There is a connection to the extent that the iron pipe through which mineral water containing hydrogen sulfide flows is graphitized, while besides iron sulfide as a corrosion product, free sulfur from hydrogen sulfide is also found.

Stumper gives no precise explanation of this corrosion process. From our investigations it appears that free sulfur suspended in water, in the presence of metallic iron, aggressively attacks the latter. This will be discussed in Chapter VIII.

In the literature available to us, apart from P. Medinger, H. D. Holler (3) also gives a reason for the fact that corrosion of iron takes place in the ground when air is excluded. According to Holler, breakdown of water is the only possible means by which enough oxygen is formed to oxidize the iron present in his experiments. Holler concludes on the basis of the above considerations that in the absence of an adequate supply of air in the ground the oxygen, necessary for the oxidation of the iron in the cases he mentions of iron corrosion, must be provided by the breakdown of water. Although Holler does not expressly so state, it

appears from his discussion that he is thinking of the water as broken down into H_2 and O_2 , as in the case of electrolysis of water. But since both in his laboratory experiments and in the ground, according to the current electrochemical view, galvanic action is possible, while electrolysis, the way in which he conceives of the breakdown of water, cannot occur and must be regarded as incorrect.

On the basis of Holler's iron corrosion experiments, in which the development of hydrogen occurs from mixtures of soil, iron powder, and water, we might draw the conclusion that a piece of iron, in the absence of air but otherwise under normal conditions in the ground, undergoes corrosion accompanied by development of hydrogen. From our observations it appeared that a difference exists between the corrosion of iron in a finely divided state and of a massive piece of iron. In the former case, hydrogen gas is formed by iron powder with water rich in salts in the absence of air, while in the latter case under the same conditions, no hydrogen development was observed by us. The performance of this last-mentioned experiment for cast iron is described on page 14. It is therefore not permissible to declare Holler's explanation, of the corrosion of iron powder with development of free hydrogen gas, valid for the corrosion process of massive iron, and this experiment must therefore never serve as an interpretation of the corrosion of cast-iron pipes in a neutral soil in the absence of air.

Like Medinger, Holler has failed to prove by laboratory test the cause assigned by him for the graphitization of cast iron.

Dr. C. M. Wichers (4) in her study of the influence of hydrogen ion concentration on the corrosion of pipes in the ground in the province of Groningen was unable to draw any definite conclusion, since the corrosion of cast iron was encountered both in acid and in alkaline soils, -- an observation which will later (page 36) be seen to be in agreement with our own. She also mentions sulfate reduction, on the basis of a previous publication of one of the present authors (5), in connection with the presence of iron sulfide in the ground, and states the possibility that this iron sulfide may be both a product of the corrosion of the iron and an original component of the soil. In this connection Dr. Wichers on page 123 makes the observation "das Sulfatreduktion an sich keine Grundursache fur die Korrosion zu sein braucht." /German: "that sulfate reduction need not be a primary cause of the corrosion."/

The author explained on page 120 that her conclusions were of a provisional nature and that there was a possibility that they could be proved by further investigations. Our own investigations in this field, which are discussed in detail below, have shown that sulfate reduction plays both a special and an important part in cast-iron corrosion, from which it appears that Dr. Wichers's opinion quoted above is untenable.

In another publication in which the same author again deals with corrosion of cast iron she says: (6) "Obviously in very corrosive soils incipient corrosion can be practically brought to a standstill if the ground is packed so tight and hard around the pipe that the access of water and oxygen is adequately blocked," and also, "Even when the soil which firmly and tightly surrounds the pipe is saturated with water, the danger of corrosion in my opinion is not increased, since no circulation of the water and the air around the pipe takes place." /The quotations are in German./ From this it is evident that she is of the opinion that oxygen is necessary to the process of corrosion of cast iron in the ground, while from our observations it appeared that great corrosion of cast iron took place in the presence of iron sulfide and hydrogen sulfide and therefore in the absence of oxygen in the ground. This is analyzed in greater detail in Chapters IV and V of the present article.

Chapter II. Description of the Phenomenon of Corrosion of Cast Iron in the Ground.

In a period of a good three years a great number of cases of corrosion of pipes and relevant soil material have been studied, from different types of soil from all over the province of North Holland. The pipes affected were all from sections of the province where there were no electric rail lines, so that stray currents cannot have been the cause of the corrosion. In all the corroded pipelines it could be seen that the corrosion had taken place only from the outside in, as is clearly seen in the accompanying illustration (Figure 1), so that in looking for the cause of the corrosion the soil surrounding the pipes must be taken into account.

Judging by the outside of the affected pipes three different forms of corrosion may be distinguished, viz.:

- a) Graphitization,
- b) Rust formation,
- c) Graphitization and rust formation.

a) By graphitization, also referred to in the literature as spongiosis and iron canker, is understood the change undergone in corrosion only by cast iron, in which the iron changes into a soft mass which on close examination appears to contain black lead or graphite, whence the name of the corrosion process. The term "spongiosis" refers to the porous nature of the affected cast iron, while the name "iron canker" alludes to the rapid proliferation with which the corrosion spreads.

An example of graphitization is shown in Figure 2. This pipe, from a pipe failure, has a diameter of 150 mm and lay for eight years in a heavy, grayish-blue clay soil in Dirkshorn, in the district of Harenkarspel. In order to show up the graphitized spots, the pipe was turned a little on

the lathe, so that the dark, corroded places stand out clearly against the shiny surface of the iron. In this way even an incipient graphitization can be made visible, as will be seen from the illustration. A soil sample taken from the immediate vicinity of the corroded pipe was found on examination to be rich in iron sulfide; this also explains the darker spots present in it. This case of iron corrosion forms a typical example of the rich pipe graphitization material that has been studied in the laboratory. In some graphitized pipes, iron sulfide is found as a crust over the surface, with the graphitized spots beneath it. By far the greatest part of the material studied showed the appearance already described, while cases of corrosion of types b) and c) occurred only sporadically.



Figure 1



Figure 2

b) Of the corroded pipes studied, a few examples showed ordinary rust formation over their surface. In the case of one pipe which had lain for about 50 years in very dry dune sand, the sand crust around the pipe contained only iron rust, so that the rusting process had evidently been caused by access of air and moisture. Where the metal was affected in this way we never found a corroded hole. When such pipes were turned on the lathe slight graphitization showed up under the rusted spots.

c) This form of corrosion occurs in cast iron when the forms of corrosion mentioned under a) and b) alternate. In one case studied a crust was found around the pipe made up of iron sulfide and soil containing

rust, which gave a sour reaction. When turned on the lathe a pipe affected in this way shows the familiar picture of graphite spots on the shiny iron.

Of the three forms of corrosion described in the soil of North Holland, the case described under a), often coupled with a break in the pipe, occurs overwhelmingly often, in fact to such a degree that cast-iron corrosion presents a very monotonous picture.

In conclusion it must be pointed out that in case a) the iron sulfide found in the immediate vicinity of the corroded pipe, by analogy with the iron rust found near the pipe in case b), must be regarded as a product of corrosion. From the fact, too, that the original soil contains much less iron sulfide than is present near the graphitized pipe, the conclusion must be drawn that the iron sulfide comes from the corroding iron. We may regard the circumstance that iron sulfide is a product of the corrosion as a key that will enable us to solve the problem of the graphitization process.

The occurrence of iron sulfide in the soil in general and its presence near and against the corroding places on the iron pipes will be analyzed in more detail in the following chapters.

Chapter III. Sulfate Reduction and Its Occurrence in Nature.

The regular occurrence of iron sulfide as a corrosion product of iron pipes constitutes an indication that hydrogen sulfide must be involved in the iron corrosion process in one way or another.

As early as 1895, Prof. Dr. M. W. Beijerinck (8) ascribed the formation of hydrogen sulfide and iron sulfide in soils in the absence of air to the activity of a microbe of strictly anaerobic life processes, called by him Spirillum desulfuricans, later, Microspira or Vibrio desulfuricans, which is capable of reducing the sulfates present to hydrogen sulfide. This process was labeled by Beijerinck with the name of "sulfate reduction." Later he added (9), "For the time being my Spirillum desulfuricans is thus the only known agency by which sulfate reduction takes place." /Quoted in German./

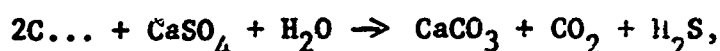
From the circumstance that iron sulfide occurs as a corrosion product of iron pipes in the ground in the absence of air and the fact that sulfate reduction also occurs here -- the only known process in the soil by which hydrogen sulfide is formed -- the conclusion is warranted that there must be a connection between the anaerobic iron corrosion process and sulfate reduction.

We must subject this last mentioned very widely occurring biological process in the soil to a more thorough discussion, as it has seemed

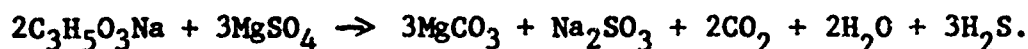
to us that to a great many this process is, if not unknown, at least unfamiliar. First of all we present the conditions, apart from the presence of moisture, which must be met to effect sulfate reduction, and which according to Beijerinck's study are:

- 1) Complete absence of air (oxygen).
- 2) Presence of assimilable organic compounds and the necessary mineral substances (physiological elements).
- 3) Presence of sulfate.

Since there is practically no soil in which the sulfate-reducing spirilla are lacking, whenever the above-mentioned conditions are satisfied the sulfate reduction process will take place. For the empirical equation of sulfate reduction according to Beijerinck the following scheme holds good:



where C ... represents the source of carbon. According to Eng. A. van Delden (10) sulfate reduction with sodium lactate as a nutrient medium runs according to the equation:



From a recent study by J. K. Baars (11), however, it appears that the actual chemistry of sulfate reduction is more complicated, in that fatty acids also occur as end products of the dissimilation process. To the question of whether we are dealing with different species of sulfate-reducing microbes the answer is that they may be considered as adaptation forms of one single plurivalent species.

As an exothermic process, sulfate reaction through oxidation of the organic food by the bound oxygen from the sulfate gives off energy which is used physiologically by the sulfate-reducing spirilla.

As to the chemistry of sulfate reduction, Baars (12) applies to it the line of thought of the two researchers Kluyver and Donker (13), who had shown the validity of Wieland's theory of true biological oxidation for various microbiological processes.

According to them the living protoplasm constitutes the catalyst which has the power to cause the hydrogen from the nutrient medium to change places. This breaks down every biochemical process into a series of monomolecular oxido-reductions. In this way an agreement is obtained with the new observation in the chemical field that multimolecular reactions do not occur.

In connection with this, according to Baars (14), in order to get a true insight into the nature of sulfate-reduction chemistry we must replace the above-mentioned multimolecular concepts with a reaction scheme, the mechanism of which outlines in four successive primary reaction steps, which result in the following equation:



With the above conception of the sulfate reduction process it thus becomes clearly evident that the bound or atomic hydrogen from the organic food is oxidized by sulfate oxygen into water. We might now wonder whether molecular hydrogen can also be oxidized into water by means of sulfate reduction. To this question M. Stephenson and L. H. Stickland (15) have given an affirmative answer. We were able to confirm their result in a simple manner.

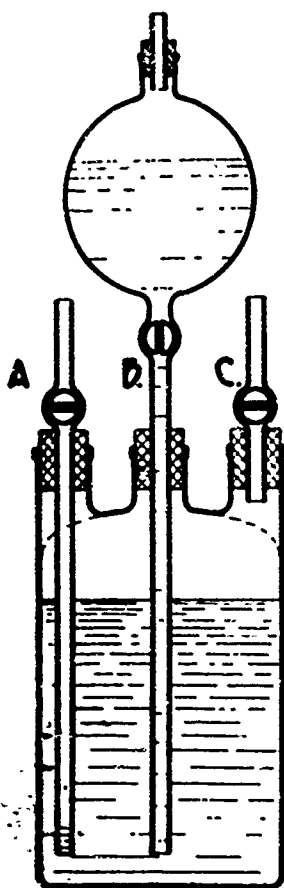


Figure 3

This method has the advantage that any leaks developing during the experiment will be immediately apparent.

For that purpose we made use of the following apparatus. In one neck of a three-necked 1-liter Woulfe jar a 250 cm³ separatory funnel is fixed with a one-hole rubber stopper in such a way that the tube reaches to the bottom of the jar. In the same way the other two necks are fitted with a two-way cock, as shown in Figure 3, cock A reaching nearly to the bottom of the jar and cock C ending flush with the stopper.

For the experiment the separatory funnel is wholly filled and the jar 4/5 filled with fresh canal water which as a rule contains sulfate-reducing spirilla. Then the air present in the jar is completely replaced by hydrogen gas. This is done by running the gas in through cock A with cock C open and the separatory funnel closed until the exchange has taken place. Then cocks C and A are closed by turns, while cock B is opened. In the experiment, set up by us in this way, sulfate reduction, recognized by a black coloration of the liquid caused by the formation of iron sulfide coupled with a definite reduction in the volume of hydrogen became visible after one week.

Instead of keeping cock B open throughout the experiment, one may keep it closed at the beginning and afterwards open it periodically. It will then be seen from the inflow of fluid into the Woulfe jar that a decrease in hydrogen has created a vacuum.

It may be remarked in connection with the above experiment that it has not been shown that the sulfate-reducing microbes alone have had the oxidizing effect, since canal water was used, in which all sorts of bacteria occur, while in apparent contrast to this Stephenson and Stickland in their experiments made use of a pure culture of sulfate-reducing spirilla. That our test and that of the two researchers named are practically alike will be more fully shown in Chapter V. In Chapter II it was pointed out that iron sulfide as a corrosion product would point the way to solution of the problem of graphitization of cast-iron pipes. It has already been shown above that sulfate reduction is capable of forming iron sulfide in the process of corrosion of iron in the absence of air. The fact that graphitization was found by us in several hundred cases in cast-iron pipes, the ground in contact with the pipe being involved in sulfate reduction, leads one to suspect that this graphitization and sulfate reduction side by side have some connection with each other. The widespread occurrence of sulfate reduction in the soil of North Holland need cause no surprise at all, if we follow the history of its development over the past centuries. For this low-lying land has several times been flooded by the sea, so that larger or smaller parts of it lay under water for considerable periods. In this watery country naturally enough a luxuriant plant life developed, especially in the many lakes, ponds, and puddles, where the water and the silt left behind contain the necessary nutritive elements for vegetation. For many centuries, generations of these water plants succeeded each other, the dead plants sinking to the bottom of the water and thus causing an accumulation of organic materials that we find today in our peat deposits. Where silt was deposited on the ground in these repeated floodings a soil was also formed that is rich in organic material, which we find now as clay soils. The accompanying maps (Figures 4a and 4b) of North Holland at different periods show clearly how the greatest part of this province, which formerly consisted of great expanses of water, has been changed into land by alluvial deposits and by reclamation.

If we check whether the subsoil of North Holland formed in this way meets the requirements set on page 8 for the occurrence of sulfate reduction, we find this to be the case in every respect.

For by the piling up of organic matter in the form of silt and dead plants as a dense mass and by the high ground-water level, condition 1) is satisfied, namely complete absence of air (oxygen). At the same time, condition 2) is fulfilled, namely the presence of assimilable organic compounds and of the necessary physiological elements. Since the ground-water present comes in part from sea water of high sulfate content, condition 3), too, namely the presence of sulfate, is fulfilled. Of course this discussion has no bearing on the sandy strip of dune land in North Holland, which is of entirely different origin.

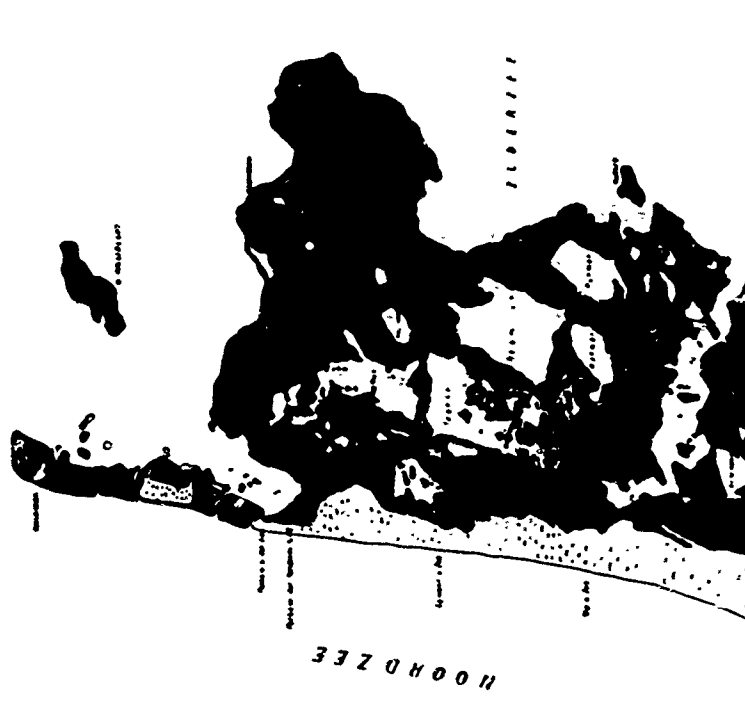


Figure 4A. North Holland about 1300.

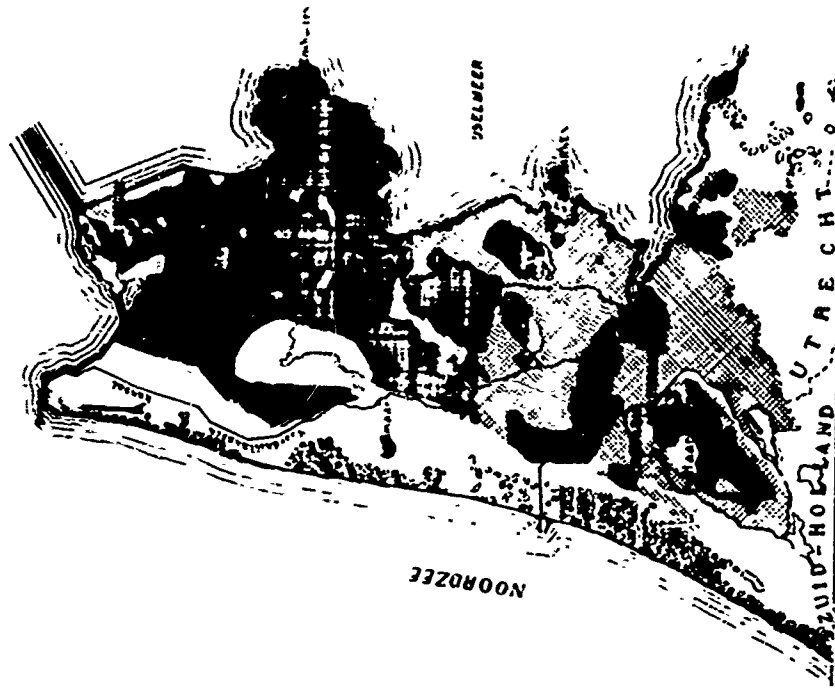


Figure 4B. North Holland in 1934.

What has been said of the province of North Holland with regard to sulfate reduction applies of course to all areas of the earth of the same origins. How widely these sort of soils occur in which sulfate reduction prevails, can be seen from what Beijerinck (8) says in the work already mentioned. According to him the formation of hydrogen sulfide and other sulfides under the influence of life is a natural phenomenon of great extent, and the great mass of these sulfur compounds derive from the reduction of sulfates. He further points out that iron sulfide occurs widely on loamy seacoasts that are alternately dry and flooded, and also in the mud of swamps, ponds, and streams, the development of which under the influence of life is generally recognized. To this we may add, from the direct observation of one of us (16), that sulfate reduction occurs very generally in the soil of the tropics and has been made the subject of a study.

From the above it does seem clear that sulfate reduction is one of the commonest and most extensive microbiological processes on the earth. When we think of the fact that in general the organic matter is supplied by the plant kingdom and that sulfates and mineral components are present as a rule in every soil, then it becomes understandable that sulfate reduction is encountered all over the earth, if under these circumstances we also have an absence of atmospheric oxygen. This last is true even at a slight depth in the ground when the soil is of dense composition, as is usually the case with clay and peat soils. It may also be mentioned as a noteworthy fact that sulfate reduction is found at very great depths. In a drilling made at Bennebroek on 6 February 1931 to obtain water, at 71 meters below the surface a gray-green clay was found, a sample of which obtained under aseptic conditions was found upon close examination to contain sulfate-reducing spirilla.

From this example it seems that when the conditions for sulfate reduction already mentioned obtain, then sulfate reduction will take place at practically unlimited depths in the ground. Our studies done on the significance of sulfate reduction in the process of iron corrosion and the results obtained from them are described in the following chapters.

Chapter IV. Consideration of the Possibility that Hydrogen Sulfide from Sulfate Reduction is the Cause of Iron Graphitization.

The fact that hydrogen sulfide aggressively attacks iron is generally known.

Since the soil in cases of graphitization of cast-iron pipes always appeared to contain iron sulfide, especially in the vicinity of the corrosion spots, this sulfide cannot have originated otherwise than by the effect of hydrogen sulfide, which according to Beijerinck (8), as mentioned above, comes from nothing else than sulfate reduction. Obviously the idea suggests itself of attributing the graphitization of cast-iron

pipes in the ground to the aggressive action of hydrogen sulfide derived from sulfate reduction. On this hypothesis three articles have already appeared, entitled "Sulfate Reduction as Cause of Corrosion of Iron Pipelines" (17), "Some Important Microbes in the Waterworks Department" (18), and "Serious Corrosion Processes in Lead and Iron Water Pipes" (19). The first article concerned a study made in 1923 of a dug-up 9-inch main of drawn iron of the Municipal Waterworks of Amsterdam, which had been laid on the bottom of the Y-harbor in 1908 and in 1923, i.e. after having been exposed to the constant influence of sea water for 15 years, had to be replaced with a new pipeline because of numerous leaks. Upon inspection on the spot the old pipe appeared to be covered over its whole surface with blue-gray mud from the Y-harbor, which owed its color to the presence of iron sulfide. The covering of the pipe, consisting of a layer of jute impregnated with mastic was entirely gone in some spots, so that it was possible that at those spots corrosion by the biogenous hydrogen sulfide could take place unimpeded at the expense of the iron of the wall of the pipe, which in turn was so weakened in spots by the process that finally it could no longer resist the internal water pressure and gave way at the corroded spots. The holes that developed in this way in the wall of the pipe even attained a diameter of 2 to 3 cm.

In the second article, too, attention was called to the destructive effect of biogenous hydrogen sulfide on iron pipelines in the ground in North Holland, emphasis being laid on the fact that in this region, as in some other provinces, there is much peat and sea-clay in the soil and also that the ground water is often brackish, so that it possesses a higher sulfate content than fresh water. Moreover, readily assimilable organic compounds may also occur in abundance.

Since in both peat and clay soils at some depth all the conditions of life for the strictly anaerobic sulfate-reducing bacteria are as a rule fulfilled, it need cause no surprise that in those soils sulfate reduction is often spontaneously encountered, recognizable by its dark color, caused by iron sulfide, while less often the odor of free hydrogen sulfide is detectable, as was very plainly observable in the peaty earth at Assendelft at a freshly dug trench for a pipeline in November 1929.

The third article was a communication on the cause of graphitization of cast-iron pipes. Graphite formation in cast-iron pipes is presented in that article as a result of the influence of hydrogen sulfide formed by sulfate reduction. At the same time attention is called to the fact that in the process of corrosion of cast-iron pipes in the ground by sulfate reduction it is chiefly accidental damages to the protective asphalt coating of the pipeline that constitute the first point of attack, the graphitization then taking place by taking iron out of the cast iron. In the last-mentioned article, from the identity of behaviour of cast iron with respect to sulfate reduction and to the ordinary corrosion by hydrogen sulfide in the laboratory, insofar as only graphitization is considered, the conclusion was drawn that graphitization in general is

caused by an acid, and in the ground with air excluded it was caused in all the cases observed by hydrogen sulfide from sulfate reduction. It was further affirmed that under this circumstance it may be regarded as out of the question that any other acids in the ground besides hydrogen sulfide can occasion the formation of graphite. Carbonic acid turned out under investigation not to be capable of it, or at least not to an appreciable extent, while the other soil acids, under the anaerobic condition of the ground in question, are much less strong than hydrogen sulfide.

Upon examination of a number of cases of graphitization of cast iron it appeared that the chemical effect of hydrogen sulfide on the iron could not be the cause of corrosion.

Extreme cases of corrosion occurred in soils which, apart from the soil immediately surrounding the corroded iron pipes, contained little or no sulfides. On the one hand the hydrogen sulfide derived from the slight sulfate reduction that originally prevailed in the ground could for that reason not have caused the extreme corrosion by itself. On the other hand it seems, to judge by the layer of high iron sulfide content, found directly around the corroded pipes, that the extreme corrosion was caused by hydrogen sulfide. In this last case, however, this attack by hydrogen sulfide derived from sulfate reduction should have produced hydrogen gas, but according to laboratory tests such is not the case. It follows that a purely chemical effect on the cast iron by hydrogen sulfide formed by sulfate reduction cannot be the cause of the graphitization. This will be gone into in detail in Chapter V. Nevertheless, an important share in the corrosion process must be conceded to sulfate reduction, since, as was shown on page 7 above, iron sulfide was always found as a corrosion product of the iron. The following test also shows that sulfate reduction is involved in the anaerobic corrosion process. To perform this test, a cast-iron pipe half a meter long and 12 cm in external diameter was lathed shiny for 2/3 of its length and placed in a glass cylinder. This cylinder was entirely filled with canal water, that was rich in salts with a neutral reaction, and was closed airtight with a glass cover fitted with a device for collecting any gas that might be formed. The test took place in the dark at room temperature and lasted two months. At the beginning a little iron rust was formed by the oxygen present in the liquid. Throughout the test no gas was formed, and for the first month no change was observed in the iron. During the second month a black coloring appeared both on the surface of the iron and in the liquid, due to the formation of iron sulfide, caused by the sulfate reaction that took place after the first month. This experiment performed with a partially graphitized cast iron surface gives the same result just described.

The conclusions from these tests, which were repeated several times, are:

- 1) That a piece of solid iron in a neutral-reacting electrolyte with air excluded results in no visible hydrogen gas development and does not corrode;
- 2) That a piece of solid iron in the presence of sulfate reduction under the same conditions as named under 1) results in no visible hydrogen gas development, but does corrode, with iron sulfide appearing as a corrosion product;
- 3) That the graphite formed in a natural way, which contains fine particles of iron in a metallic state, in the test described does not yield visible hydrogen gas development, in contrast to cast-iron powder.

On the basis of the above it was necessary, in further investigation of the cause of graphitization of cast iron in the ground, to try to place the part that sulfate reduction plays in this corrosion process in a proper light.

Chapter V. The Significance of Sulfate Reduction in the Process of Iron Corrosion in the Ground.

Before going on to report the experiments that open up insight into the part played by sulfate reduction in iron corrosion in the ground, it is necessary to point out that in these experiments we always started with raw cultures of the sulfate-reducing microbes, since these experiments after all come down to an "accumulation test" according to Beijerinck (20) which from a practical point of view can be considered valid for pure cultures. The principle of the accumulation test, of course, is aimed at furthering the special conditions of development of specific microbes and thus causing them to get the upper hand over all others. It is not only in the laboratory, but also in nature that according to the principle of the accumulation test one species of microbe comes to the fore and is thus in a position to practice its own specific activity. Therefore when the above-mentioned conditions for sulfate reduction are realized in the ground, according to the principle just discussed, only the sulfate-reducing spirilla will accumulate in the ground and sulfate reduction will be the one prevailing process. From this consideration, it follows that results obtained with sulfate-reduction accumulation tests in the laboratory have the same validity as for soils that are characterized by sulfate reduction.

In order to find out whether the chemical hydrogen-sulfide corrosion of cast iron coincides in all respects with that which is caused in an accumulation test of sulfate reduction, the following comparative experiments were undertaken.

a) In the first experiment a piece of cast iron was put into an aqueous solution of hydrogen sulfide saturated at room temperature. A definite development of hydrogen takes place, while the liquid slowly acquires a black color from the iron sulfide given off. After a considerable time the surface of the cast iron shows a layer of graphite as a soft mass, which could be easily scraped off with a knife. In addition, to avoid confusing the graphite with iron sulfide, the graphite formed was proved chemically.

b) In the second experiment any gas development can be expected only after some weeks, inasmuch as it is dependent on the growth of the hydrogen-sulfide-forming sulfate-reducing microbes. In view of the longer duration of this experiment it was therefore necessary to use an apparatus to capture any gas formed, so as to prevent its escaping observation. For this a wide-mouthed 250 cm³ glass bottle was closed with a single-hole rubber stopper fitted with a glass tube with a bulge near its lower end on which a cast-iron ring rests, the tube reaching almost to the bottom of the bottle. A bottle thus equipped was completely filled with ground water, and, on repetition of the experiment, with canal water and soil. In the last case the bottle was 3/4 filled with earth that had appeared corrosive, further completely filled with ground water and a layer of kerosene oil was laid on the meniscus of the water in order to prevent its evaporation. The apparatus is shown in Figure 5.

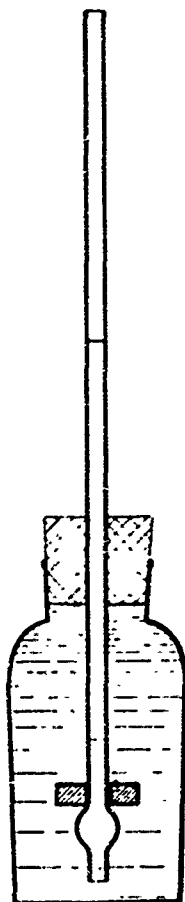


Figure 5

During the time of the experiment the meniscus level of the water in the tube remained unchanged, from which the conclusion was drawn that, both before and after the onset of sulfate reduction, which was observed after about a week, recognizable by the black coloring of the soil and the liquid by the iron sulfide formed, no gas development took place.

At the end of the experiment a layer of graphite appeared to have formed on the surface of the cast-iron ring, just as described under a). If the metallic iron had in this case been attacked solely by hydrogen sulfide, as in the first experiment, then all the iron affected would have been converted into iron sulfide, so that the ratio of the affected iron to the iron sulfide would have been 1:1. But upon investigation this ratio was found to be greater than unity. (See page 21.) The differences that exist between these two types of cast iron corrosion are shown in the table below.

Cast Iron Corrosion by H_2S : Case A	Cast Iron Corrosion by Sulfate Reduction: Case B
1. Development of H_2	1. No development of H_2
2. $\frac{Fe}{S} = 1$	2. $\frac{Fe}{S} > 1$
3. Graphitization	3. Graphitization

It appears from this that the only agreement between cases A and B consists in graphitization, and that otherwise the way that the iron is corroded is fundamentally different.

The graphitization brought about in cast iron by sulfate reduction therefore cannot be the result of simple hydrogen sulfide influence. But of course the possibility must not be ruled out that in swamps and stagnant bodies of water sulfate reduction may prevail to such an extent that sufficient free hydrogen sulfide is present to bring about a chemical corrosion of the iron.

In cases of cast iron corrosion, in the ground of North Holland, investigated by us, only exceptionally, free hydrogen sulfide was detected in accompanying soil and water samples, so consequently we dealt nearly exclusively with cast iron graphitization not caused by chemical hydrogen sulfide attack.

To show plainly that sulfate reduction plays a special part in cast-iron corrosion, the corrosion process in question in the ground was reproduced visibly by means of a laboratory experiment. The following experiment was used for that purpose.

Three large sterile test tubes were filled more than halfway with sulfate-reduction agar according to Delden's formula (21), except that the more strongly alkaline-reacting sodium lactate was replaced with calcium lactate and a small quantity of iron sulfate ($FeSO_4 \cdot 7 aq$) was added. Filling the test tubes to a high level with the agar medium ensured that anaerobia would prevail in the lower portions, as required for sulfate reduction.

In tube number 1 is put a cast-iron rod, and the whole tube is afterwards sterilized. The contents of tubes 2 and 3, previously sterilized, are inoculated with a culture of sulfate-reducing spirilla, the infection of the two being made equal (by filling them with nutrient agar that will just pour, and which has been infected shortly before), and a cast-iron rod is placed in number 3 (just as in number 1). Kept in a constant-temperature bath at $30^\circ C$, after four days tube number 3 showed a very definite dark precipitation of iron sulfide, beginning around the iron rod, showing that sulfate reduction had set in. Tube number 2 after the same lapse of time showed no iron sulfide formation, indicating that sulfate reduction had not yet begun. The same was true of tube number 1, since its contents were sterile and so even after several months showed no

iron sulfide formation, while the cast-iron rod, to judge by external appearances, had undergone no change. Fourteen days after the beginning of the experiment tube number 2 began to get dark from beginning sulfate reduction, while tube number 3 at the same time was of a very dark color around the iron and also showed formation of iron sulfide above the iron.



Figure 6

In Figure 6 from left to right are shown tubes 1, 2, and 3 seventeen days after the beginning of the experiment. The conclusion is that in tube number 3 because of the presence of metallic iron not only did sulfate reduction begin ten days earlier than in tube number 2, but also proceeded much more intensively, with corrosion of the iron. As for tube number 1 in comparison with tube number 3, it appears that without the microbiological process of sulfate reduction no iron corrosion occurs. From the tests made it appears clear that sulfate reduction fills a special role in iron corrosion, which will be further discussed. That the presence of metallic iron greatly promotes sulfate reduction was confirmed by a number of tests made on that point. These tests were done as follows: with various media, including, besides the usual sulfate-reduction agar, ground water, canal water, and without metallic iron and when necessary inoculated with sulfate-reducing spirilla. The tests with metallic iron always gave decided sulfate reduction earlier than those without iron. At the same time it was observed that no difference in results existed between the tests done with water and with various sorts of soil, from which it follows that the outcome of tests with fluid cultures may also be regarded as valid for the ground under natural conditions.

In various experiments we therefore made use of fluid cultures, as they are more conveniently available for examination than soil cultures. In connection with the role that iron plays in sulfate reduction, consisting in promotion of that process, the question suggested itself to us whether we are concerned here with a specific property of iron or a more general property of the metals. To find an answer to that question the above-described agar test of tubes 2 and 3 was done in completely filled and well-stoppered tubes, each containing a rod of the metal to be tested. In this way we tested: wrought iron, cast iron, lead, copper, aluminum, and zinc. From this orientational experiment, which was continued for several weeks, the impression was obtained that although iron promotes sulfate reduction much more strongly than any of the other metals named, this property is not specific for iron alone. As has already been remarked on page 16, in iron corrosion under the influence of sulfate

reduction, more iron in ferrous form is found as a corrosion product than iron sulfide accounts for. In order to get a clear insight into the chemistry of the corrosion process it was necessary to conduct experiments to determine quantitatively the corrosion products in the form of iron sulfide and those in the form of ferrous compounds.

For this purpose narrow-mouthed half-liter stoppered bottles, after the introduction of small pieces of cast iron weighing a total of 0.5 to 1 gram, were completely filled with oxygen-free canal water or ground water, which seemed from previous tests to bring about sulfur reduction readily even without intentional inoculation. The iron content of the water used was measured colorimetrically to be taken into account in later computations.

In these tests it is desirable that the water used be oxygen-free, to prevent the iron's being a little rusted by the oxygen, in which case a correction would be necessary for the corroded iron. The oxygen in the water would also have to be measured in order to make it possible to make the correction in question. Difficulties were encountered in eliminating oxygen by chemical means because addition of oxygen-binding chemicals affected the test unfavorably. The simplest and most promising method of getting rid of the oxygen appeared to us to be the application of a biological method according to which the narrow-necked bottles completely filled with water are allowed to stand, well sealed, for a few days in the dark at room temperature. After that time the water appears on examination to contain only traces of oxygen, which can be disregarded in the experiment. The bottles thus prepared are, after introduction of the iron, placed in a constant temperature bath for several weeks at 30°C. As a rule the corrosion of the iron by this time is promoted to such an extent by sulfate reduction that one can proceed to the quantitative determination of corrosion products, namely iron sulfide and other ferrous compounds.

Now the sulfide formed and the amount of iron corroded must be determined. The sulfide is partially present in solution and partially precipitated on the piece of iron. In the liquid, after the sulfide, the iron is measured and also the iron sulfide that has adhered to the iron along with the sulfide that is derived from the iron.

For measuring the sulfide we made use of a flask fitted with a three-hole cork. Two glass tubes were run through the holes, one of which almost reached the bottom of the flask to admit washed carbon dioxide, and the second, which ended just below the cork, served to carry off hydrogen sulfide formed from the iron sulfide and the carbon dioxide. The third was fitted with a funnel for pouring in dilute sulfuric acid.

To perform the analysis, the material containing sulfide was put into the flask and the flask closed with the three-hole cork. The sulfide that had adhered to the piece of iron was loosened as much as possible by rinsing as the fluid was poured in and thus gotten into the fluid. To prevent oxidation of the sulfide by the air, the latter must be removed as quickly as possible. The outlet tube was now connected

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with a pair of wash bottles connected in series and provided with a measured volume of silver nitrate solution of known strength. Five minutes after the carbonic acid stream, uninterrupted throughout the experiment, had been passed through the apparatus, 100 cm³ of sulfuric acid (1 : 4) was introduced through the funnel into the flask to break down the sulfide. The process was carried on with gentle heat until no more hydrogen sulfide escaped. Measurement of the sulfide in the fluid took a couple of hours, while for the pieces of iron it lasted some six hours. The silver nitrate solution in which the hydrogen sulfide generated was captured was freed of silver sulfide by filtration; the excess silver nitrate was titrated back into an aliquot part of the solution by Volhard's method.

In the liquid remaining in the flask, the iron content was determined by gravimetric methods as Fe₂O₃. By this method silicic acid can be precipitated with the iron, so that this must be taken into account.

The piece of iron with sulfide adhering was treated in the same way for measurement of the sulfide. After the metallic iron was completely dissolved, the test was continued until no more hydrogen sulfide escaped. To measure the blank, a piece of the same cast iron was treated in completely the same way.

To illustrate the way in which the ratio of the total ferrous iron to the iron sulfide formed was determined, we present the following set of figures from one of the analyses performed as an example.

For a test at 30°C. which lasted for six weeks, the required figures were as follows:

Contents of the bottle 500 cm³.

Original iron content of the water 0.20 mg/l.

Weight of the cast iron used 1 gram.

The quantity of silver nitrate consumed by the hydrogen sulfide developed in a blank experiment with 1 g. of cast iron was 0.70 cm³ 1/10 normal.

Computation

Hydrogen sulfide from iron + adhering iron sulfide uses up 6.19 cm³ of 1/10 N silver nitrate.

Hydrogen sulfide from pure (blank) iron test 0.70 cm³ of 1/10 N silver nitrate.

Hydrogen sulfide from iron sulfide adhering to the iron (6.19 - 0.70) 5.49 cm³ 1/10 N silver nitrate.

Hydrogen sulfide from sulfide in the solution uses up 1.54 cm³
1/10 N silver nitrate.

The quantity of iron in the solution is 37.08 mg Fe.

The quantity of iron from the sulfide found is $5.49 \times 2.8 = 15.37$
mg Fe.

Total quantity of iron is $(37.08 + 15.37) = 52.45$ mg Fe.

The total quantity of corroded iron is

$$52.45 - \frac{0.20 \times 580}{1000} = 52.45 - 0.12 = 52.33, \text{ rounded off } 52.3 \text{ mg Fe.}$$

Total quantity of iron from sulfide is $(5.49 + 1.54) \times 2.8 = 19.68$,
rounded off 19.7 mg Fe.

$$\frac{\text{Total Fe}}{\text{Fe from Fe S}} = \frac{52.3}{19.7} = \frac{2.7}{1}$$

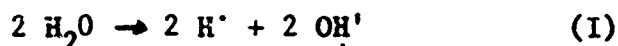
A number of analyses done in the manner described above gave the
results shown in the accompanying table.

No.	Total quantity of corroded iron (Total iron)	Quantity of iron from iron sulfide	Total Fe Fe from FeS
1	10.6 mg	3.9 mg	2.7 : 1
2	9.8 mg	3.0 mg	3.3 : 1
3	12.6 mg	3.8 mg	3.3 : 1
4	13.6 mg	4.0 mg	3.4 : 1
5	39.3 mg	16.0 mg	2.5 : 1
6	26.6 mg	11.1 mg	2.4 : 1
7	52.3 mg	19.7 mg	2.7 : 1
8	5.7 mg	1.8 mg	3.2 : 1
9	6.5 mg	2.4 mg	2.7 : 1
10	4.6 mg	1.8 mg	2.6 : 1

From these figures it seems clear that in the corrosion of iron under
the influence of sulfate reduction the greatest part of the iron is not
bound as sulfide. The conclusion already drawn (page 17), that anaerobic
iron corrosion does not take place directly through hydrogen sulfide,
is therefore proved by these figures.

If we bear in mind that in the above tests the pH of the corrosive water was between 7 and 8, we rule out the possibility that the degree of acidity is the cause of the iron corrosion, and beside, the corroded iron is not bound as sulfide. If we consider iron corrosion in the same corrosive water that was concerned in the above tests, but with access to air, then this appears to take place intensively, the reaction product being iron rust.

Since the water used is a very dilute salt solution, it forms the electrolyte in which according to the current electrochemical view anodic iron solution takes place; this may be represented schematically by the following equations:



The reaction of equation (II) is for the sake of brevity represented as a process in which the charge of the hydrogen is transferred to the iron, so that the latter goes into solution. In reality the iron is ionized by the electrolytic solution pressure, according to Nernst. By reason of the fact that iron has no homogeneous composition, the heterogeneous particles will necessarily act in an electrolyte as galvanic cells, the metallic iron in the so-called "corrosion cell" as anode forming the solvent electrode. The H-ions of equation (I) are discharged on the cathode, which is polarized by the hydrogen being released.

Electrochemistry teaches that this reduces the potential difference between cathode and anode of the corrosion cell, which may even drop to zero. That this last is the case in the iron-corrosion cell appears from the observation repeatedly made by us that in laboratory, tests of corrosion an iron rod, in a neutral electrolyte, comes to a standstill if oxygen is excluded.

If oxygen is again admitted, corrosion begins again, as is electrochemically explained by attributing the role of depolarizer to the oxygen (22). The reaction that takes place here is:



The fact that through depolarization, the anodic solution of the metal -- in our case iron -- takes place uninterruptedly in the corrosion cell, is of great importance here. If iron corrosion takes place uninterruptedly when air is excluded, then the oxygen must of necessity have been replaced by another depolarizer.

Various chemical substances can readily serve as hydrogen acceptor or depolarizer. In a special case bound oxygen may perform this function. In the anaerobic corrosion tests in the laboratory in the presence of sulfate reduction, the corrosion of iron continued uninterruptedly as long

as sulfate reduction was active, while no development of hydrogen gas could ever be detected, since in the sealed test bottles no change in pressure occurred.

Since in these anaerobic tests no other hydrogen acceptor than the sulfate oxygen is present, the latter must have served as depolarizer in the iron corrosion process. In this connection let us refer again to the experiment of M. Stephenson and L. H. Stickland mentioned earlier (page 9) in which they showed that in sulfate reduction the sulfate oxygen is capable of oxidizing hydrogen gas.

Our conclusion that in the iron corrosion process in the presence of sulfate reduction the sulfate oxygen acts as depolarizer is thus supported by the observation of the two authors named.

As to the manner in which the cathodic hydrogen is transferred in the sulfate reduction process to the sulfate oxygen, i. e. the way in which the depolarization of the cathode of the corrosion battery is accomplished, we must refer to a study by B. Elema (23) of denitrification in connection with the occurrence of an oxidoreduction potential in the process, which shows an analogy with sulfate reduction, in which he indicates a reversible oxidoreduction system which he calls a bio-indicator, formed in the metabolism process, as the carrier.

According to Nernst (24), in the corrosion cell, anodic iron solution will progress in the electrolyte if the potential of the iron:

$$E_{Fe} = - \frac{0.0002}{2} T. \log \frac{P_{Fe}}{P_{Fe..}} \quad (A)$$

is more negative than the hydrogen potential against solution:

$$E_H = - \frac{0.0002}{2} T. \log \frac{K'_H C_{H_2}}{(C_H.)^2} \quad (B)$$

In the two formulas E_{Fe} and E_H represent the potentials, T is the absolute temperature of the electrolyte, P_{Fe} the electrolytic solution pressure of the iron, $P_{Fe..}$ the osmotic pressure of the ferro-ions, K'_H a constant, C_{H_2} the concentration of polarizing hydrogen, and $C_H.$ the hydrogen ion concentration.

The value of E_{Fe} is as large a negative value as possible when $P_{Fe..}$ is as small a value as possible. In the anaerobic iron corrosion process with sulfate reduction, the corrosion products $Fe(OH)_2$ and FeS have a small solubility product (25), so that the value of $P_{Fe..}$ is small and therefore E_{Fe} assumes a large negative value. The smaller negative the hydrogen potential E_H is, the more favorable the functioning of the corrosion cell will be. In the corrosion process in question, the

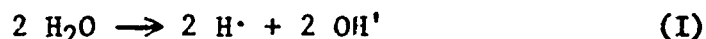
reaction of the solution appears to remain practically neutral, so that the value of C_H in (E) is to be regarded as constant. The value of E_H is therefore determined solely by C_{H_2} and is as small a negative value as possible when C_{H_2} is as small as possible. Keeping the C_{H_2} value small is done by depolarization, which in the above-mentioned corrosion process is carried on intensively by sulfate oxygen.

In the next chapter an analysis will be given of the chemistry of the anaerobic iron-corrosion process with sulfate reduction.

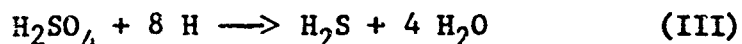
Chapter VI. The Chemistry of the Anaerobic Iron-Corrosion Process with Sulfate Reduction.

From what was said in the foregoing chapter the conclusion must be drawn that the iron corrosion discussed there is to be regarded as an electrochemical process, with sulfate reduction filling the role of depolarizer, or in other words an electro-biochemical process.

This process, as far as anodic iron solution is concerned, was shown schematically on page 22 by the equations:

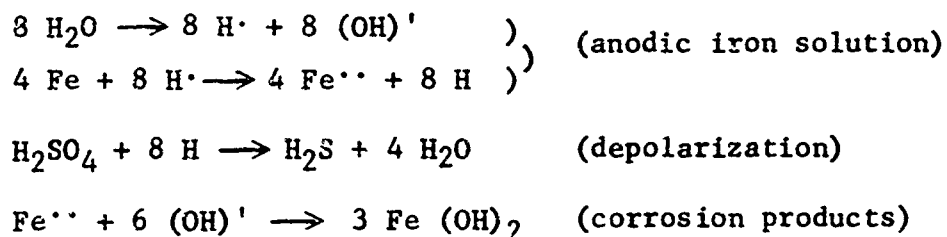


The biochemical part of the corrosion process, namely sulfate reduction, which accomplishes the depolarization, is represented on page 9 by the equation:

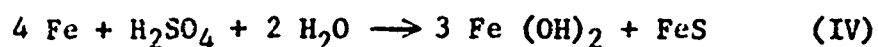


It is obvious that the hydrogen released in (II) in connection with the assumed presence of sulfate reduction is oxidized according to (III) by sulfate oxygen, while the hydrogen sulfide formed in this process combines with the iron given off by (II) to form iron sulfide.

Stoichiometrically the whole electro-biochemical process of iron corrosion may be represented by the following equations:



By counting up we obtain from the foregoing equations the empirical molecular equation for the chemistry of corrosion:



From this equation it follows that the ratio between the total quantity of corroded iron and the portion of it that is represented by iron sulfide must be 4 : 1. Quantitative iron-corrosion tests with sulfate reduction in closed bottles to determine the ratio just reported are described on page 19, and the table showing the results obtained is given on page 21.

From these figures it appears that the above-named ratio is not constant, but is always found to be lower than 4. The cause of this difference between the theoretical and the experimentally obtained values for the ratio may be sought in the circumstances that in the sulfate reduction process besides the oxidation of the cathodic hydrogen there is always organic material oxidized as food, with liberation of hydrogen sulfide as a dissimilation product. The result is that more iron sulfide is formed than there otherwise should be merely from (IV), so that a value smaller than 4 must necessarily be found for the above-mentioned ratio. It seemed to us that when one particular type of water was used in the iron corrosion tests with sulfate reduction, the ratio found was fairly constant, but that it varied with different types of water. Thus in tests 2, 3, and 4 of the table on page 21 for one and the same type of water a constant ratio of about 3.3 was found, while with another type of water in tests 5, 6, and 7 the ratio was about 2.5. This observation suggests that the nature and quantity of organic matter in the water influences the ratio in question. The above discussion leads to the conclusion that the ratio figure 4 is to be regarded as a limit value.

For the sake of clarity let us review once more what arguments have led to the conception presented here of anaerobic iron corrosion chemistry; these arguments may be summarized as follows:

- 1) Since anodic solution of a piece of metallic iron in an electrolyte always takes place in the presence of a depolarizer, then iron corrosion in the absence of air, if no hydrogen is developed, can take place only if the oxygen of the air is replaced by another depolarizer.
- 2) In anaerobic iron corrosion with sulfate reduction a depolarizer must be present, since according to the experiments no hydrogen is produced.
- 3) Since in the ground or in water in the absence of sulfate reduction no anaerobic corrosion of a piece of metallic iron takes place, but begins only with sulfate reduction, the sulfate oxygen must be considered as the depolarization in the corrosion cell.

- 4) In the anaerobic iron corrosion process iron hydroxide and iron sulfide are the corrosion products, the ratio between the total of ferrous compounds formed and the iron sulfide being greater than 1.
- 5) The above-mentioned corrosion process takes place in a milieu whose practically neutral reaction does not change significantly during the process.

The empirical molecular equation for the chemistry of anaerobic corrosion of iron, obtained from the simplest reaction equations, which account for the five points given above, is presented in the reaction scheme (IV).

Chapter VII. The Process of Iron Corrosion with Sulfate Reduction in the Laboratory is the Same as Anaerobic Iron Corrosion in the Ground

In the foregoing chapters it has been shown that iron corrosion can be brought about in the laboratory in an electrolyte in the absence of air with the help of sulfate reduction.

If we compare the anaerobic iron corrosion process in the ground with the laboratory experiment, the latter seems, as far as the phenomena are concerned, to be a complete reproduction of the former. For in both cases the corrosion products consist of iron compounds which because of the prevailing anaerobiosis occur only in the ferrous form, namely iron sulfide and a ferrous compound that can be no other than ferrous hydroxide. In both cases the corrosion takes place in a reaction which, as is reported on page 36 of some of the cases investigated, is practically neutral, without any gas formation occurring. In the corrosion of cast iron in both cases graphite is formed. The complete correspondence as to corrosion phenomena in the laboratory experiment and in the ground leads to the conclusion that the iron corrosion process in the laboratory with sulfate reduction and the anaerobic iron corrosion process in the ground are equal to each other.

The fact that the iron corrosion process can be produced by means of a laboratory experiment in which solutions are used exclusively justifies the conclusion that in the corrosion process in the ground the ground water serves as electrolyte and nutrient medium of the sulfate-reducing spirilla; this must be recognized as of fundamental significance.

Graphitization of cast iron, as a special case of the process of iron corrosion in an anaerobic soil, is according to the foregoing to be regarded as an electro-biochemical process, which, as has already been reasoned in detail, consists of an anodic solution of the iron in which sulfate reduction fills the role of depolarizer.

Since the iron corrosion experiments in the laboratory were carried out in closed bottles, the sulfate reduction that took place in them had of necessity to come to a stop because of exhaustion of the food supply, so that the corrosion process came to an end for lack of a depolarizer. It seemed possible to us, however, to make such a change in the apparatus for the corrosion experiments that the corrosion could continue indefinitely. The experiment was set up in a tall glass cylinder with ground rims, 58 cm high and 20 cm in diameter, which was provided with a tube at the bottom. This was closed with a stopper fitted with a drain tube with a cock. After the cast-iron test specimens were placed on the bottom of the cylinder the cylinder was completely filled with ground water or canal water and then closed with a glass plate in such a way that no air bubbles remained under the plate. The experiment ran at room temperature, and, for reasons to be explained later, it was necessary for it to be set up in the dark.

The oxygen present in the water is used up partly by the rusting of the iron and partly by the aerobic microbes always present in the fluids used, so that the necessary anaerobia for sulfate-reducing bacteria is brought about. As a rule after a few days the beginning of sulfate reduction is detectable by the black coloring of the water by the formation of iron sulfide. Exclusion of light is necessary to prevent the development of other microbiological processes that unfavorably influence the growth of the sulfate spirilla. In any case excluding the light prevents any complication in the anaerobic iron corrosion process, whereas it results in identity of conditions with those in the ground as far as light is concerned. After the fluid was involved in intensive sulfate reduction the water in the cylinder was refreshed weekly. This can be done most carefully by removing the glass plate, letting about a liter run off through the drain tube, and then filling the cylinder completely with fresh ground water or canal water and closing it again with the plate in the same way as before.

Because of the new food material supplied periodically with the water, the sulfate reduction remained uninterrupted. At the same time it appeared that the prevailing anaerobic condition in the fluid was not in the least disturbed by the periodic refreshing.

The specimens that were subjected to the continuous anaerobic corrosion experiment consisted of pieces of cast-iron pipe 10 cm in length with an external diameter of 6.5 cm. These test pipes had been cleaned completely on the outside by turning on a lathe and afterwards covered with a coating of asphalt. Letters were cut into the coating, so that at those places the bare iron was visible. After the corrosion test described above had run for six months with these cast-iron specimens, the original bare places in the form of cut-out letters were covered with a thick layer of corrosion material which was black from iron sulfide.

Beneath this layer the cast iron appeared to be graphitized to a depth of 1/2 to 1 mm. From this result it therefore seemed that by means of the experimental procedure described the graphitization of cast iron can be effected continuously, so that here just as in the ground an uninterrupted corrosion is obtained.

It seemed to us on several times repeating the above experiment that the results were by no means always equally strong as far as graphitization is concerned. This seems in retrospect not surprising, since every time a new anaerobic corrosion experiment is set up the biological and physiological factors as a rule will differ from those of earlier experiments, and the amount of sulfate reduction and therefore the amount of graphitization are dependent on those factors. This last is in conformity with what is observed in practice concerning the graphitization of cast iron. It often happens that pipelines are weakened after only a few years by the graphitization process, while in other cases this takes place only after decades. This point will be discussed in more detail in later chapters.

Chapter VIII. The Iron Corrosion Processes Encountered in Waterline Practice, Considered from the Electrochemical Point of View, Do Not Differ Essentially from Each Other.

In Chapter II the cases of corrosion occurring in waterline practice were discussed briefly. After the analysis of anaerobic corrosion with sulfate reduction in the foregoing chapters it has now become possible to present a more detailed discussion of the various forms of corrosion and their mutual relationships. Superficially one would think, to judge from the different external appearance that the corroded pipe in each of the three cases mentioned in Chapter II assumes, that in each case we have to do with a different cause as well.

But this may be ruled out on the basis of electrochemical findings about metal corrosion, for electrochemistry teaches that every corrosion of metal is an anodic solution of the metal. On that basis the differences observed in the various cases of corrosion are to be explained from the circumstances under which the corrosion took place. If we consider the differences in the three cases mentioned, they are, as far as the corrosion products observed are concerned, in the case mentioned under a), iron sulfide and ferrous hydroxide, which are deposited against the ground surrounding the pipe. In the case described under b), the corrosion product consists of ferric hydroxide, the common yellowish-brown iron rust. As to the case reported under c), the corrosion products constitute a mixture of the iron compounds mentioned under a) and b), occurring mixed with soil components as a hard crust attached to the pipe. This crust formation, which also takes place in the ordinary rust process in the ground, must be attributed to oxidation of the originally formed ferrous

into ferric compounds. The same hard crust may be obtained by mixing moist sand with ferrous compounds in the form of iron sulfide or ferrous sulfate and leaving the mixture to dry exposed to the air.

The formation of iron sulfide and iron hydroxide in case a) in contrast to the formation of iron rust in case b) is to be explained as follows from the prevailing circumstances in the ground: For case b) the ground is in quite aerobic condition, so that the iron going into solution anodically in the ferrous form is oxidized by the oxygen of the air into the ferric state. In case a) the ground is in a completely anaerobic condition, so that the ferrous compounds formed cannot be further oxidized, while the presence of iron sulfide is simply a result of the fact that the sulfate reduction process accomplishes the depolarization in the anodic solution of the iron, the hydrogen sulfide formed precipitating a part of the dissolved iron as iron sulfide. In the intermediate case c) the stage occurs in which because of varying ground conditions (lowering of the water level, drying out of the ground) an originally anaerobic corrosion process of an iron pipeline was followed by a corrosion process with access to air. Iron sulfide formed in an anaerobic state will then be converted into acid ferric sulfate, so that the anodic solution of the iron now takes place in the presence of a high hydrogen-ion concentration, and the corrosion naturally progresses faster than before, when the air still had no access. Of course all this can only happen when the ground has no excess of lime.

If during the above-mentioned acid formation, anaerobic conditions again set in, the degree of acidity would gradually decline, because of the iron solution process among other things. This would again result in a pH favorable to sulfate reduction, so that this could again take place. In this stage of the corrosion process c) it is no longer possible to discern that a temporary aeration coupled with acid formation has taken place.

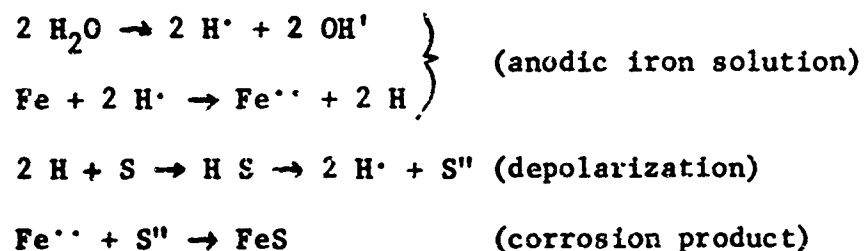
Soils containing iron sulfide will also give an acid reaction upon aeration, because of oxidation of iron sulfide to acid-reacting ferric sulfate.

We were able to find this fact confirmed by observations in the laboratory. Soil samples kept in glass pots, which originally reacted neutrally or slightly alkaline and at first were in a condition of intensive sulfate reduction, after a few weeks of contact with the air showed a strong acid reaction. This laboratory experience is a case of acid formation in the ground by oxidation of iron sulfide (derived from native iron compounds by sulfate reduction) to acid ferric sulfate just as in the iron corrosion in the intermediate case c), with this difference, that in case c) the iron sulfide was derived from the pipe and in the other case from the iron compounds almost never lacking in any soil.

Dr. D. J. Hissink (26) points out that acid formation by oxidation of accumulated sulfides where there is a shortage of bases in the ground can result in high degrees of acidity (pH usually 2 to 3, but sometimes even zero or a negative figure). If an excess of lime is present, gypsum and iron oxide will be formed from the ferric sulfate.

In the foregoing discussion of the three cases of corrosion mentioned it was always possible on the basis of the electrochemical conception of the anodic-solution of metallic iron to account for the observed differences from the circumstances. Since these circumstances determine the depolarizer necessary for each of the three cases of corrosion, in case a) with exclusion of air sulfate oxygen will constitute the depolarizer with the help of sulfate-reducing bacteria, while in case b) with access of air the atmospheric oxygen acts as such. In case c) with alternate anaerobia and aerobia the bound sulfate oxygen and the free atmospheric oxygen act by turns as depolarizer. It appears from this, then, that there is essentially no difference between the three forms of corrosion considered.

In the cases of iron corrosion in the ground discussed, oxygen always served as depolarizer. In investigating in the laboratory the degree of corrosion of different makes of cast iron under the same conditions, we also made use of hydrogen acceptors other than oxygen as depolarizers. Sulfur seemed to us to be a powerful depolarizer, as could be shown by a very simple test. In a wide-mouthed 250 cm³ stoppered bottle entirely filled with a suspension of flowers of sulfur in distilled water was placed a cast-iron rod. The bottle was sealed airtight. After it had stood for several hours it could be observed by the black coloring by iron sulfide that iron corrosion had begun. After a few weeks it was plain to see that the cast-iron rod was graphitized, for a layer of graphite could be scraped off it with a knife. The same test carried out with a piece of wrought iron also showed definite corrosion after a few weeks. From the electrochemical point of view of corrosion the process in question may be represented as follows:



This process of iron corrosion with sulfur as depolarizer is important in connection with the observation of R. Stumper (2) already mentioned, who had observed graphitization in a cast-iron pipe through which mineral water flowed containing not only hydrogen sulfide but also sulfur set free from the hydrogen sulfide, as can easily be done by oxidation. It is true that hydrogen sulfide is capable of effecting graphitization of cast iron, but this is less powerful than the corrosion effected by sulfur.

Stumper's report that the detached crust contained, in addition to iron sulfide, 70-90% free sulfur makes it probable in connection with the result of iron corrosion with sulfur as depolarizer reported above that the graphitization process observed by Stumper was chiefly effected by sulfur in the same way.

In connection with the fact that sulfur can be aggressive with respect to iron it might also be mentioned that according to the literature (27) the formation of free sulfur can occur in nature through biological action and therefore iron corrosion caused by sulfur may be encountered. The literature (28) also reports the occurrence of a microbe, Thiobacillus thiooxydans, which can convert free sulfur present in the ground into sulfuric acid, while the microbe itself can exist in solutions of up to 5% sulfuric acid. Where there are acid soils the possibility cannot be ruled out that the acid formation in such corrosive soil took place in that manner.

In cases of corrosion besides the differences that have been discussed there is also a similarity, namely graphite formation in cast iron, which is also to be explained by the circumstance of the peculiar composition of the iron.

From the point of view of the electrochemical manner of solution of the iron we should not be surprised that graphitization in the general sense of the word is found in graphite-rich cast iron and that it occurs in both aerobic and anaerobic corrosion of such iron. That in fact graphitization takes place in the corrosion of cast-iron pipes in the presence of air, too, both in the ground and in the open atmosphere, is easy to show by cleaning pipes rusted in this way with a file or turning them a little on a lathe, so that the dark graphite spots stand out against the shiny iron surface. That the dark spots actually contain graphite can be brought out in the following way:

- 1) The dark scrapings, resembling pencil lead when heated on a sheet of platinum with potassium chlorate or nitrate give an explosive combustion which points to graphite.
- 2) A dark, shiny dust comes off the dark spots on the fingers. The dark spots on the pipe can be polished to the well-known graphite sheen.

But the term graphitization is only used in the narrower sense of the word to denote cases of corrosion of cast iron in the ground where the formation of graphite is very pronounced, as has already been discussed in detail in Chapter II under a). It is this form of corrosion of cast iron that we have been particularly investigating. The result of our investigation, set down in the foregoing chapters, is that this graphitization is an electro-biochemical process which occurs only in anaerobic soils.

By explaining the likenesses and differences encountered in the cases of corrosion discussed from the prevailing conditions in which the attack on the iron took place, we have from the electrochemical point of view reduced the cause of corrosion in all corrosion processes to the anodic solution of iron with a certain depolarizer.

Chapter IX. The Concept of "Aggressiveness" of Soils, Acquired According to the New Insight into the Anaerobic Process of Iron Corrosion.

Up to now in investigation of the aggressiveness of soils with respect to iron pipelines an opinion has been given on the basis of chemical analysis of the soil sample concerned. As a rule the reaction and the moisture content of the soil sample are also determined, and then in further chemical studies the dry soil material is used. To the chemical analyses were later added measurement of the electrical conductivity and the pH index of the soil moisture, after we had come to see the importance of these quantities in appraising the aggressiveness of the soil.

In spite of extensive physical and chemical researches on soil, it has not been possible to explain cases of apparent aggressiveness with respect to iron on the basis of the results of those researches. An exception must be made for soils of a pronounced acid character, where in respect to iron we are dealing with a purely electrochemical manner of attack. Appraisal of such a soil with respect to such aggressiveness, because of the simplicity of the case, offers no choices, but in our experience such cases rarely occur. We have been confronted almost exclusively with cases where the ground was extremely aggressive toward iron, as could be seen from the graphitization of cast-iron pipes, which caused them to fail even within a few years, while according to the above-mentioned soil analyses these soils should have been of the most innocent nature.

That in the cases of soil aggressiveness with respect to iron that we are talking about the usual physical and chemical examination was inadequate to give an explanation of the aggressiveness of the soil is to be blamed on the circumstance that we were groping in the dark for the cause of that aggressiveness. The result was that the most important studies to determine the aggressiveness in the cases mentioned above were never made. As has been explained in the foregoing chapters, the iron corrosion process concerned is of electro-biochemical character, so that to determine the aggressiveness of the ground with respect to iron the performance of a micro-biological examination is necessarily required.

As we have explained in the foregoing chapters, the graphitization of cast iron is completely dominated by the microbiological process of sulfate reduction. The aggressiveness of the soil is therefore determined by its capacity for reverting to sulfate reduction in the presence

of metallic iron and is thus dependent on all the factors that are of influence on the life and activity of the sulfate-reducing spirilla. There is no need of further proof that sulfate reduction as a completely anaerobic process is dependent on the absence of air, the presence of suitable organic materials and necessary mineral constituents, with the "minimum law" of course having its effect.

As to the intensity of the sulfate reduction process, it is determined not only by the suitability and quantity of the necessary organic and mineral food constituents, but also by the activity of the sulfate-reducing spirilla, and this in turn is determined by various circumstances, such as the salt concentration of the medium and the strain of spirilla most prominently present, which must be regarded according to Baars (29) as an adaptation form of one single species. Still another special circumstance that may come to the fore is the density of the ground, which may partially or wholly prevent the supply of new food, so that the process of sulfate reduction is braked or completely stopped. The frequent apparently conflicting cases where observed differences in degree of iron corrosion encountered in practice cannot be traced back to the physical and chemical character of the ground may find their explanation in the above-mentioned very diverse factors, which, as has already been explained, can be present with sulfate reduction as a life process in the ground. When conditions in a soil are otherwise favorable for sulfate reduction, the sulfate content naturally will be a criterion for the aggressiveness with respect to iron. In general, in the past no aggressive character with respect to iron has been attributed to the sulfate content in the ground, because of the chemically indifferent character of the neutral sulfates. As far as we know, the first investigator who attempted to make a connection between iron graphitization and the sulfate content of the ground was Medinger, whose work was mentioned on page 2.

The aggressiveness of the ground which follows from the sulfate present in it makes it desirable to refer to it, as distinct from other forms of aggressiveness, as "sulfate aggressiveness."

But it must also be kept in mind that in this sulfate aggressiveness two types are to be distinguished, namely:

- 1) Sulfate aggressiveness in which microbiological sulfate reduction is involved (biochemical sulfate aggressiveness);
- 2) Sulfate aggressiveness of a purely chemical nature (chemical sulfate aggressiveness).

The aggressiveness named under 1) exists both for iron and for the roots of the higher plants. In such aggressiveness with respect to iron, as we already know from the foregoing, sulfate oxygen, by means of sulfate reduction, acts as depolarizer in the iron corrosion process. Another form of sulfate aggressiveness with respect to iron sets in when, after

sulfate reduction, aeration takes place in the presence of iron or iron compounds, since from the iron sulfide previously formed, acid ferric sulfide is now formed, which splits off to sulfuric acid working corrosively not only on metallic iron but also on such building materials as concrete, cement, eternite, etc. The aggressiveness toward plant roots mentioned above must be sought in the prevailing anaerobia and the formation of hydrogen sulfide in sulfate reduction (30), while in the above-mentioned acid formation by aeration the sulfuric acid formed is also aggressive toward roots of plants. Dr. J. M. Van Bemmelen (31) has already called attention to this aggressiveness with respect to the roots of plants. According to him the formation of hydrogen sulfide and iron sulfide in the ground are caused by rotting plant material or other organic substances, by which both the gypsum and the iron oxide present are converted into iron sulfide and calcium carbonate. As to the acid formation mentioned, Van Bemmelen notes that it has already been explained by Prof. Van Kerkhoff that acid soils contain iron vitriol, which presumably developed from iron sulfide by oxidation, while the iron sulfide is a product of organic substances from peat, iron rust from clay, and gypsum from seawater. No further proof is needed that these references are to nothing else than the sulfate reduction process in the ground, followed or not by oxidation of the resulting iron sulfide under aeration, with the formation of acid ferric sulfate.

The aggressiveness mentioned under 2) represents the chemical effect of the sulfate on building materials such as concrete, cement, eternite, etc. Concerning this H. Klut (32) has the following to say: (quoted in German).

"A high content of sulfates and magnesia compounds in the water, say from 300 mg/l of SO_3 and 300 mg/l of MgO , has a particularly disadvantageous effect on mortar. The destructive effect of sulfuric acid salts on mortar is attributable to the fact that the sulfuric acid of these compounds first forms gypsum with the calcium and this gypsum then unites with the calcium aluminate present in the mortar to form a double compound, calcium sulfoaluminate, which crystallizes with a great deal of water. The great space demand made by this compound causes the gypsum to blow, its very powerful crystallization pressure bursting the mortared joints with extremely great force. In the trade, calcium sulfocarbonate often bears the unsatisfactory name of "the cement bacillus."

J. Tillmans (33) expresses himself very similarly to Klut concerning the aggressive effect of water containing sulfates on mortar, and adds: (quoted in German) "Ground water of high sulfate content is chiefly observed in peaty strata, where oxidation of the iron pyrites present into sulfate and free sulfuric acid occurs.

"The free sulfuric acid combines with the bicarbonates of the water, so that in such water commonly only a slight alkalinity is found. If more free sulfuric acid is formed than can be neutralized by the

alkalinity present, the soil becomes acid, and an especially rapid destruction of the concrete by free sulfuric acid occurs." "Where the destroyed concrete shows no acid reaction, but considerable amounts of bound sulfuric acid are found in the concrete, such blowing phenomena are present, caused by neutral water containing gypsum."

The purely chemical sulfate aggressiveness named under 2) is sufficiently illustrated by the two quotations. To determine the sulfate aggressiveness of a soil as described under 1), which may be useful if iron pipes have to be laid in it, the following procedure should be applied.

It has been fully explained above that sulfate reduction can occur in a soil or ground water when several conditions already mentioned are simultaneously satisfied.

In order to determine in the laboratory whether a soil is sulfate-aggressive in the above sense, i.e. exhibits biochemical sulfate aggressiveness, the soil to be investigated was placed by us in its original condition in a wide-mouthed flask which was completely filled with it.

Bright wrought-iron or cast-iron plates or rods are stuck into this soil and the bottle is closed and placed in the dark. After the lapse of a few weeks the test specimens are taken out for examination as to whether corrosion has taken place. The result of such a test with aggressive soil is shown in Figure 7, where the graphitization on the cast iron can be clearly seen as dark spots.



Figure 7

A clean metal surface is necessary not only in order to observe small changes -- which stand out clearly against it -- but also to ensure close contact of the metallic iron with the moist soil, which promotes the onset of the corrosion process. Upon finding the specimen not corroded after some weeks, the test can be continued for a longer period. This corrosion test was set up by us in such a way that several similar test specimens could be simultaneously put into the soil and taken out after varying periods of time, amounting to weeks or months, for observation of any corrosion that might have set in. In judging the results of corrosion tests in the laboratory, carried out in closed spaces, it must always be taken into account that the conditions are not entirely in conformity with reality. For natural conditions in the ground are subject to fluctuations, i.e., all factors on which sulfate reduction is dependent, such as anaerobia, moisture content, and the amount of food, may vary, either to the advantage or to the disadvantage of the biological process concerned. It follows from this that in laboratory tests as to the aggressiveness of the soil, we are entirely dependent on the moment when the soil sample was taken, so that the result of the test may come out too favorable or too unfavorable and so not give a true picture of the sulfate aggressiveness of the soil.

This does not alter the fact that the laboratory test described is as a rule a serviceable method by which the aggressiveness of the soil can be judged. It is desirable, however, especially when the laboratory test shows no aggressiveness, to acquaint oneself with the local character of the soil from a biological point of view, in connection with sulfate reduction.

It is possible to make tests in the ground in order to study its aggressiveness under natural conditions, this procedure is, in the nature of the case, to be preferred to the laboratory test. Instead of iron test pieces it is then convenient to make use of whole sections of iron pipe, of small diameter, lathed clean, which can then be put into the ground to be tested at the desired depth.

In determining soil aggressiveness it is worthwhile to take into account the type of soil as to density and organic content, as well as pH, electrical conductivity, sulfate content, and the organic matter content of the ground water. The following table represents a few soils which have appeared to work aggressively on iron pipes.

Study of Biochemically Sulfate-Aggressive Soils
Samples Taken 1 June 1933

No.	Origin	Type of Soil	Soil		Conduc- tivity ⁶ K ₁₈ ·10 ⁶	Soil Moisture		
			Free H ₂ S	Bound H ₂ S		pH	SO ⁴ mg/l	Organic Matter Content*
1	Edam	Clay	neg.	neg.	2722	6.7	716	327
2	Broek in Waterl	I } II } III }	neg.	pos.	4244	7.4	316	250
3			neg.	Weak pos.	4811	7.1	27	240
4			Strong pos.	Strong pos.	3381	7.1	161	156
5	Oostzaan	Peat	neg.	Strong pos.	1740	6.7	189	421
6	Wormer	Peat	neg.	Strong pos.	1050	6.5	trace	130

* According to Schulze-Trommsdorff.

One might think that when a soil under natural circumstances shows little sulfate reduction or none at all, while appearing to offer the conditions favorable to it, that soil should be regarded as non-aggressive. That this opinion is not justified appears from many cases in practice, as was pointed out on page 14 and as will be seen from numbers 1 and 3 of the above table, where graphitization of cast-iron pipes

occurred in soils that contained little or no hydrogen sulfide or other sulfides, and so by themselves showed little or no sulfate reduction. This may be explained by the property of metallic iron already discussed of going into solution anodically and thus forming hydrogen, as indicated in the corrosion equations (I) and (II) in Chapters V and VI; in other words metallic iron can act as a hydrogen donator, which, as we have reported above in Chapter IV, strongly promotes sulfate reduction and in the above-mentioned soils induces sulfate reduction. It follows from this that although the soil is not originally aggressive in itself, it can become so when metallic iron is added to it. In practice this occurs in laying asphalt-covered iron pipes, in case the protective coating is so damaged that at those places a metallic contact with the soil moisture occurs. It is particularly for such soils that the above-described test with metallic iron is very necessary. The mutual influence that metallic iron and sulfate reduction exert on each other makes it necessary to make special requirements for the protection of iron pipelines that are laid in such soils.

The next chapter will go into this matter more fully.

Chapter X. Discussion of Pipe Material and Its Protection in Connection with Soil Aggressiveness.

It was ²³pointed out in the introduction that it was necessary to have insight into the nature of corrosion before being able to take effective measures to combat the danger of corrosion. Since the study carried out has revealed the particular significance that metallic contact of the iron pipe with the soil can have in connection with corrosion, it is clear that this indicates, as far as protection of iron is concerned, the requirement that it be capable of preventing metallic contact with the soil.

In the first place the protective material must be proof against all aggressive soil influences that may possibly occur.

In the second place the protective layer applied to the surface of the iron pipe must be watertight.

In the third place the protective material must offer resistance to damage during the transport and laying of the pipes.

The first demand is practically satisfied, as far as our experience goes, by asphalt, which is in wide use for protection of pipes.

Attempts have been made in various ways to satisfy the second requirement in practice. The most used is asphaltting by the so-called dip method in the case of cast-iron pipes and winding with various kinds of insulation tapes. Our experience is that the dipped coatings applied

often do not meet the requirement of watertightness, while with insulation tape better results are achieved in this respect.

In testing the protective layer for the pipe the following simple method may be used. Short pieces of pipe, of small diameter, are provided with the protective layer in the factory-approved manner and completely immersed in water in a glass tank. After one or more days when held in the light the non-watertight places will show up as rusty spots, which if the test is continued longer will grow into nodules of rust. If the test is only intended to evaluate the watertightness of the protective layer on the surface of the pipe, any spots of rust appearing on the ends of the pipes may be left out of consideration.

That the dipped coatings, as they have been applied up to now, often do not satisfy the requirement of impermeability to water was apparent to us repeatedly in examination of defective cast-iron pipes that were being replaced by new ones. Aside from the defective places, it appeared when the asphalt surface was lathed away that the pipe was spotted all over its surface with little graphite spots that could only have come about because the coating applied by dipping was not watertight. These graphite spots are very clearly observable in Figure 2. Dr. Wichers (34), too, observed the nonwatertight spots in the asphaltting of pipes, described by her as follows: "The almost microscopic openings (pinholes) formed during the asphaltting process (even in the case of hot asphaltting at the factory) occur in great numbers. If the pipe is laid in clay containing hydrogen sulfide, they reveal themselves by circular spots of iron sulfide which stand out sharply against the gray color of the clay." /Quoted in German./

In spite of the fact that the coatings applied to cast-iron pipes by dipping up to now have proved inadequate as concerns impermeability to water, it appeared from our laboratory tests that the same asphalt coatings, if applied more thickly, satisfy the requirement set.

The third requirement, that of ability of the protective asphalt coating to resist mechanical damage during transporting and laying of the pipes, will in our opinion probably never be satisfied, and certainly not by the dipped coatings usual for cast-iron pipes. It may be asked why this requirement needs to be set, since any damage of the protective asphalt layer that may occur can surely be repaired after the laying of the pipes. Experience shows, however, that this usually cannot very well be done, and in any case small injuries, which from the point of view of corrosion can have the same consequences as larger ones, can very easily be overlooked.

To get around this third requirement both so-called ground improvement around the pipes and packing the pipes in clay have been suggested.

In ground improvement around the pipes, the dug trench in which the pipes are laid is filled with sand, so as to prevent contact between the pipeline and the ground, if the latter might be aggressive, so as to prevent corrosion. But if we remember that according to the results of our studies ground water is just the medium through which sulfate reduction runs its course in the ground, and it is plain that the sand brought in cannot hinder the ground water from reaching the pipe, then the anaerobic iron corrosion process can still take place, whether with more or less obstruction. It is even conceivable that anaerobic iron corrosion may be favorably affected by just this kind of ground improvement.

Attention was again called to packing the pipes in clay, in order to protect cast-iron pipes against corrosion, in very recent times by Dr. Wichers. She says: "Our investigations showed that even in very aggressive soil and in the presence of abundant moisture the speed of corrosion is so slow that it can be ignored, if only this soil is fine and surrounds the pipe very closely and tightly.

"A cheap and universal remedy against corrosion is therefore packing the pipe in a thin layer of clay or loam. Such a covering hinders the circulation of gases and water to such an extent that corrosion of the pipe is undetectable even after decades." [Quoted in German.]

As it is our experience that the occurrence of even severe corrosion of cast-iron pipes in the form of graphitization often takes place in dense clay, it seems strange at first glance that clay is recommended to protect pipes against corrosion. This seeming contradiction is explained by the circumstance that clay is found in which by exhaustion of the food originally present the prevailing sulfate reduction is brought to a stop, while because of its density no new food can be brought in. Only such clay should be considered for packing pipes. But since it is difficult to determine the suitability of clay for this purpose, by packing the pipes in a clay not thoroughly studied and approved for the purpose one would run great risk of exposing the pipes to corrosion. A study of the suitability of the clay to be used as a protective material against pipe corrosion consists in carrying out a sulfate aggressiveness test, as described on page 35. If the pipes are packed in clay they should first be provided with a dipped coating of asphalt.

As to the clay to be used for packing pipes, Dr. Wichers (35) says: "It is best to use a neutral-reacting clay or loam free of sulfates and other injurious constituents. If such material is not available; then in a case of necessity even quite aggressive soils may be used, if only they are quite dense." [Quoted in German.] It is not clear to us what the author means by the second sentence quoted, for in our opinion an "aggressive soil" can hardly be used for a pipe covering even if it is "quite dense." It is not impossible that the author's meaning is that the aggressiveness of the soil comes about very quickly, as might appear from her next article (36): "But we have found in the case of pipes that have

lain in the ground for twenty years that even in very aggressive soils and in the presence of abundant moisture the speed of corrosion is so slow that it can be ignored, if only this soil is fine and surrounds the pipe very closely and tightly." /Quoted in German./

In our opinion it is not permissible to speak of a very aggressive soil if, as the author reports, the iron corrosion that was caused by it in 20 years is negligible. According to our views on soil aggressiveness such a soil would have to be called not aggressive with respect to iron.

The difficulty of finding clay available for packing pipes which satisfies the demands made on it and the lack of certainty that the clay used cannot, under any soil conditions that may occur, lose its favorable characteristics, will stand in the way of its use on a large scale.

Where experience has taught that especially the third requirement, namely that of possessing ability to resist mechanical damage to the insulation, is not satisfied by the usual and least costly way of asphaltting by dipping, the inadequacy of this method of protection of iron pipes against the danger of corrosion in the ground is obvious.

From the study done of iron corrosion the necessity appeared clear for iron to be adequately protected if it is to be a dependable material for pipelines. Since, as has already been said, this protection encounters difficulties in practice, iron must be regarded in principle, in view of the corrosion occurring in the ground, an unsuitable material for pipes. In areas where sulfate reduction is widespread and the ground for that reason is aggressive toward iron, a pipe material must therefore be used that is not corroded in such soils. For this such materials as concrete, cement, and eternite are to be considered, which are not corroded in the ground by sulfate reduction in the same way as iron. According to Klut (37) these materials can be corroded by hydrogen sulfide and its compounds. In answer to this it may be said that free hydrogen sulfide is rarely found in the soils of North Holland, while the compound of this substance in insoluble form as iron sulfide is present and as such is unharmed. There is therefore no question of the aggressiveness asserted by Klut -- at least not for North Holland. From the nature of the case our conclusion applies in general to regions where such soils, aggressive because of sulfate reduction, occur.

Of the above-mentioned materials concrete, cement, and eternite pipes are already manufactured and are already in use in waterworks engineering. The Provincial Waterworks of North Holland has already had some experience in the use of a heavy transport line which consisted externally of reinforced concrete, covered with aluminum cement and with coal tar, the last to prevent penetration of ground water. This transport pipeline was laid in a region of North Holland consisting in part of very watery peat soil and in part of heavy and dense clay, in both of which

sulfate reduction was abundant. About five years after the laying of the pipe it was examined at several places and found to be in completely undamaged condition. Cast-iron pipes laid in this region had all gone leaky within ten years as a result of graphitization. Although pipes made of mortar, with or without the addition of asbestos, are not subject to biological sulfate-aggressiveness, still it must be borne in mind that they may be sensitive to chemical sulfate aggressiveness, as explained earlier.

In the above-mentioned case for the peaty soil the sulfate content of the ground water in which the concrete pipe was lying was 33 mg of SO_4 per liter and for the clay soil 193 mg of SO_4 per liter; these sulfate contents are too low to act aggressively on concrete, while they can maintain sulfate reduction, which is aggressive for iron. We are thus dealing with the case where the ground exhibits no chemical sulfate aggressiveness, but does exhibit a biological sulfate aggressiveness. In such cases the use of mortar pipes is indicated.

There is also the advantage that sulfate reduction, which for iron pipes was a "necessity," has been made into a "virtue" for mortar pipes, since this process constantly attempts to diminish the sulfate content in the ground.

Still, circumstances may arise in the ground where the sulfate content of the ground water is so high that there is danger of chemical sulfate aggressiveness, so that in such a case it is worthwhile to recommend that the mortar pipes be protected by asphalting against penetration by water.

One might think that damage to the protection of mortar and eternite pipes runs the same risk of corrosion as damage to the protection of iron pipes. But if we consider the common case where a pipeline must be laid through a region with a soil in anaerobic condition, whose ground water in general has a low sulfate content, but at the same time places do occur where the ground water has a high sulfate content, then for the sake of safety one should take the precaution of protecting not only iron pipes but also mortar or eternite ones throughout their length. But damaged spots on the iron pipe are exposed to corrosion throughout their length, while such spots on mortar and eternite pipes are only exposed to danger if they are in contact with ground water of too high sulfate content.

It thus appears that damage to the protected surface of mortar and eternite pipes offers far less chance for the occurrence of corrosion at the damaged place than is the case with iron pipes.

It has been found from experience that adequate protection of iron pipes against the aggressiveness with respect to iron in anaerobic soils caused by sulfate reduction is not to be achieved simply, whereas the

realization of an adequate protection is not without financial difficulty. This does not alter the fact that, now that the investigation done has brought out the necessity of devoting special care to the protection of iron pipes, there is a possibility of getting better results by that means in biologically sulfate-aggressive soils than has been the case heretofore. But in our opinion it is, from the point of view of corrosion, more economical to replace the use of iron as pipe material in the above-mentioned soils with such materials as concrete, cement, and eternite, which in contrast to iron are proof against the sulfate reduction process in the ground. This therefore provides a means of getting around the problem of biological sulfate aggressiveness in the ground as far as water pipelines are concerned.

Summary:

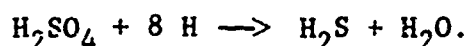
In the study of the cause of graphitization of cast iron the following results were obtained:

- 1) The only explanations and discussions of the graphitization of cast iron in the ground encountered in the literature are found upon critical consideration to be incorrect, both on the basis of the theoretical difficulties pointed out, and more especially because of the fact that no notice is taken in them of the occurrence of iron sulfide as a corrosion product, and that this cannot be accounted for by analyses presented of the corrosion process in question.
- 2) The forms of corrosion of cast iron in the ground were classified on the basis of the external appearance of the corroded pipes into:
 - a) Graphitization,
 - b) Rust formation, and
 - c) Graphitization and rust formation.

By analogy with the iron oxide found in rust formation, the iron sulfide found in graphitization was noted as a product of corrosion. This was seen as the key with which to solve the problem of the graphitization process of cast iron.

- 3) Prof. M. W. Beijerinck's study done in 1895 was cited, according to which hydrogen sulfide and other sulfides in nature are exclusively derived from biological sulfate reduction. A more thorough-going discussion of this generally occurring process was given, and at the same time attention was called to the predisposition to sulfate reduction of the subsoil of the low-lying portions of North Holland, which finds its explanation in the developmental history of this province and which from the nature of the case is also valid for similar areas elsewhere. The experiments of M. Stephenson and L. H. Stickland were also cited, which brought to light the fact, important

for explaining the anaerobic iron corrosion process, that molecular hydrogen is oxidized by the sulfate spirilla into water. Then mention was made of Wieland's theory, applied to sulfate reduction by J. K. Baars, concerning true biological oxidation, the general validity of which for microbe life had been demonstrated by Kluver and Donker, so that according to him the chemistry of sulfate reduction consisting of four primary reaction stages, may be summarized in the equation:

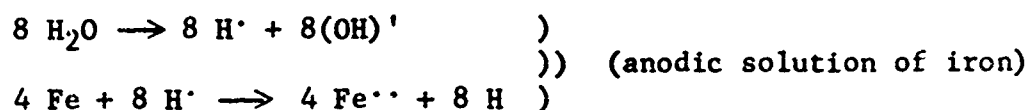


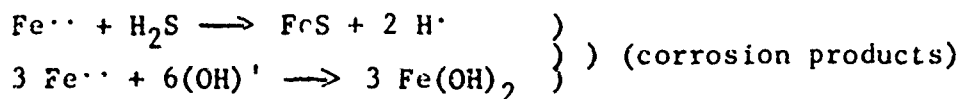
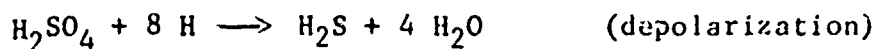
- 4) A discussion is presented of the fact that extensive corrosion of iron has been observed in soils with only weak sulfate reduction, while cast-iron pipes in such soils may when corroded be surrounded by a layer of high iron sulfide content. The conclusion is drawn from this that the graphitization process cannot be a purely chemical sulfur corrosion, while at the same time it was shown by an experiment described, that the sulfate reduction process must be concerned in the corrosion of iron.
- 5) According to the Beijerinck accumulation principle the sulfate reduction process in the ground was considered as a natural accumulation process. On the basis of this it was decided that the results obtained in corrosion tests with accumulation cultures of sulfate-reducing spirilla in the laboratory possess the same validity as those obtained with soils in which natural sulfate reduction occurs. By means of experiments described it could be shown that in chemical hydrogen-sulfide corrosion of cast iron and in its corrosion by sulfate reduction the graphitization exhibited a similarity, but that otherwise there was difference in principle in the way in which the graphitization takes place.

Further research led to the conclusion that the sulfate reduction involved in the iron corrosion process fills the very special role of depolarizer in the corrosion cell, the iron going into solution anodically. This anaerobic corrosion of iron is therefore to be regarded as an electro-biochemical process.

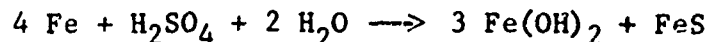
It was established from quantitative measurements that in iron corrosion experiments with sulfate reduction more iron was corroded than was found as iron sulfide. The ratio of total corroded iron to iron from iron sulfide was greater than 1 and less than 4.

- 6) It was found that the chemistry of the anaerobic iron corrosion process may be represented as follows:





The empirical molecular equation is therefore:



The ratio of total corroded iron to iron from iron sulfide which is found from this equation is 4.

It was pointed out that in the sulfate reduction process besides the oxidation of hydrogen derived from the corrosion of iron there is always oxidation of organic food material with formation of hydrogen sulfide, so that more iron sulfide is formed than would be the case according to the above equation alone, and the ratio in question must necessarily be less than 4.

The conclusion is drawn from this that this figure, in quantitative measurements to determine the ratio in question, is to be regarded as a limit value of the ratio, and therefore the observed values of the ratio, which lie between 1 and 4, were regarded as being in satisfactory agreement with the formula of the chemistry in question.

This led to the conclusion that it may be assumed that this equation represents the corrosion process with sulfate reduction.

- 7) The fact that by means of the described anaerobic cast-iron corrosion test with sulfate reduction -- as far as corrosion phenomena are concerned -- a complete reproduction is obtained of the anaerobic cast-iron corrosion process in the ground justified the conclusion that the two mutually compared processes are in fact alike. From the fact that in the laboratory experiment in question only food solutions were used, the conclusion was also drawn that in the corrosion process in the ground a fundamental importance must be attributed to the ground water as electrolyte and nutrient medium of the sulfate-reducing spirilla.
- 8) All the iron corrosion processes discussed could be reduced from an electrochemical point of view to anodic solution of iron with a specific depolarizer. The similarities and differences encountered in the cases of corrosion discussed could always be explained from the prevailing conditions under which the iron corrosion took place.

It was remarked that "graphitization" is the name for that cast-iron corrosion in the ground in which graphite formation is pronounced and which is found exclusively in anaerobic soils.

As the cause an electrochemical process was given in which microbiological sulfate reduction acts as depolarizer, so that this corrosion of iron was presented as an electrobiological process.

- 9) The aggressiveness of the soil which follows from the sulfate present in it made it desirable to designate this, as distinguished from other forms of aggressiveness, by the term sulfate aggressiveness. This was subdivided into:

1. Biochemical sulfate aggressiveness, in which microbiological sulfate reduction is involved and affects iron.
2. Chemical sulfate aggressiveness, which is of purely chemical nature and affects building materials such as concrete, cement, eternite, etc.

The procedure was given for determining the biochemical sulfate aggressiveness of a soil by means of a laboratory test by putting in the indicated way a clean piece of iron into the ground to be examined. If after a few weeks the metal surface is affected, the biochemical sulfate aggressiveness of the soil may be affirmed.

It was further pointed out that metallic iron has the property of going into solution anodically and giving off hydrogen in the process, or in other words metallic iron functions as hydrogen donator, so that sulfate reduction may be induced or if already existing strongly promoted. If therefore soils are not originally aggressive in themselves they may become so through the addition of metallic iron. It was pointed out that in practice this occurs in cases where iron waterline pipes, whose asphaltting is damaged down to the iron, are laid in the above soils and at these damaged places metallic contact of the iron with the soil is occasioned.

- 10) From the study carried out the special significance was revealed that metallic contact of the iron pipe with the ground can have in connection with corrosion. On the basis of this the conclusion was drawn that the following three demands must be made on the protective covering of iron pipes:

1. The protective material must be proof against all aggressive soil influences that may occur;
2. The protective coating applied to the surface of the iron pipe must be watertight; and
3. The protective material must be resistant to damage in transportation or in the laying of the pipes.

It was noted that the first two demands can be easily met in practice, but as to the third the opinion was expressed that it would probably never be possible to meet it, and particularly not by means of the usual dipped coatings.

A simple method was given for testing the protective coating of iron pipes for watertightness, in which a piece of pipe provided with the insulation to be tested is immersed for several days in water. If rust is formed on the surface of the protective coating, this shows that there are nonwatertight spots in the coating.

From the standpoint of the anaerobic iron corrosion process the methods of the so-called ground improvement and of packing in clay, which are used for iron pipes and with which the third demand is regarded as superfluous, were subjected to critical discussion.

After giving the reasons that iron as a pipe material must be considered in principle as unsuitable for biologically sulfate-aggressive soils, the use of concrete, cement, and eternite as pipe materials was considered the solution in these cases. The circumstance was pointed out that as far as the clay and peat regions of North Holland are concerned the chemical sulfate aggressiveness which would be injurious to the above-mentioned materials from the nature of the case seldom occurs, since in these soils the usually prevailing sulfate reduction works to diminish the natural sulfate content. This was seen as the cause of the fact that in such soils the ground water often contains little or no sulfate.

As concerns the use of concrete, cement, and eternite as pipe material, it was remarked that the possibility always exists of applying to such pipes, when they are laid in chemically sulfate-aggressive soils, the usual protective measures against corrosion.

Finally, it was pointed out that the results of the present study call particular attention to the protection of iron pipes against corrosion by the soil in general, while the use of concrete, cement, and eternite as pipe material is justified as a means of getting around the biological sulfate aggressiveness of the soil.

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